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Effects of Air Temperatures and Humidities on Efficiencies and Lifetimes of Air-Purifying Chemical Respirator Cartridges Tested Against Methyl Iodide

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Methyl iodide penetration curves through three types of respirator cartridges and canisters were determined at several temperatures to identify the significance of temperatures of testing and use. Three charcoal types showed similar results: triethylenediamine (5% TEDA-impregnated, (2% TEDA + 5% KI_3)-impregnated, and unimpregnated. Penetration curves were shifted at higher temperatures in the range 25-38° C, keeping relative humidity constant in the range 50-70%, but allowing absolute humidities to increase correspondingly. These shifts were such that penetrations were increased and service lives were decreased significantly (4-15% per °C). At constant water vapor concentration, service life of the (2% TEDA + 5% KI_3)-impregnated charcoal increased with temperature, illustrating the complexity of temperature effects. For one case (5% TEDA) using cartridges at humidity equilibrium, temperature and humidity effects were sorted out. Until these effects are better understood, air-purifying respirator cartridge and canister testing should be done at conditions more representative of possible use and at more closely controlled temperatures.

Introduction

Air purifying respirators are used at ambient air temperatures that vary widely from the 25 ± 2.5°C specified in Federal regulations for bench tests of gas and vapor cartridges and canisters.(1) Effects of temperature on efficiencies and service lives have been thought to be small, as evidenced by the range (±2.5°C) allowed for bench tests. One reported calculation, based on temperature dependence of an adsorption isotherm, has estimated 1-10% decrease in service life for every 10°C rise in temperature.(2)

Temperature effects were a concern as part of a larger project to develop criteria and test methods for certifying air-purifying respirator cartridges and canisters against radioiodine.(3,5) Such units can be potentially used at ambient temperatures above or below 25°C. In addition, heating of unequilibrated canisters was noticed when humid air was passed through them (see below). Therefore, a study was undertaken to determine the significance of temperature effects for the selected testing agent, methyl iodide.

Apparatus and Materials

The experiments were done using a Respirator Cartridge/-Canister Test System designed and built at the Los Alamos National Laboratory (Figure 1). A challenge concentration of methyl iodide in the range of one ppm by volume was generated by the flux of methyl iodide out of a standard permeation tube (Analytical Instruments Development, Inc., Avondale, PA) into an auxiliary airflow that rejoined a filtered, flow regulated and humidified air stream. The air was then heated to the desired temperature (±0.5°C) by passing it through a section of glass tubing wrapped with heating tape and insulation before passing it through the test cartridge. The cartridges were heated by incoming air only, and were not thermostated or insulated. Challenge and breakthrough concentrations were measured by a miniature gas chromatograph with dual sampling valves and loops built into a valve oven (Valco Instruments Co., Houston, TX, Model HVE-2) and an electron capture detector (Valco Instruments Co., Model 140). The ratios of these concentrations, determined by an electronic integrator (Spectra Physics, Santa Clara, CA, "Minigrator"), were combined with calibration factors to give penetration values (breakthough percentages).

Weight losses of the permeation tube and calibrated airflow rates were used to calculate challenge concentrations. Concentration control was achieved by temperature control (±0.01° C) of the permeation tube chamber, a modified valve enclosure (Valco Instruments Co., Model HVE-2). Total airflow was monitored with a hot-wire digital flow meter (Datametrics, Inc., Wilmington, MA, Model 810L). Humidification was achieved by passing air through the headspace above a stirred, heated water bath. A digital humidity analyzer (EG&G, Inc., Waltham, MA, Model 911 "Dew-all") was used to monitor (±0.2° C) both air stream temperature and dew point temperature at the test cartridge inlet. It also was modified with a relay to provide feedback to the water bath heater to maintain a preset relative humidity (±1%). Gas chromatograph/valve oven, permeation tube oven, and air stream temperatures were all controlled to preset values by using Valco Instruments Co., Model ITC-D10-399 controllers.

One type of cartridge containing a 5% by weight TEDA-impregnated charcoal (Scott Health/Safety Products, South Haven, MI, Model 642-TEDA-H), one type of canister containing a 2% TEDA + 5% KI_3-impregnated charcoal (Mine Safety Appliances Co., Pittsburgh, PA, prototype), and one

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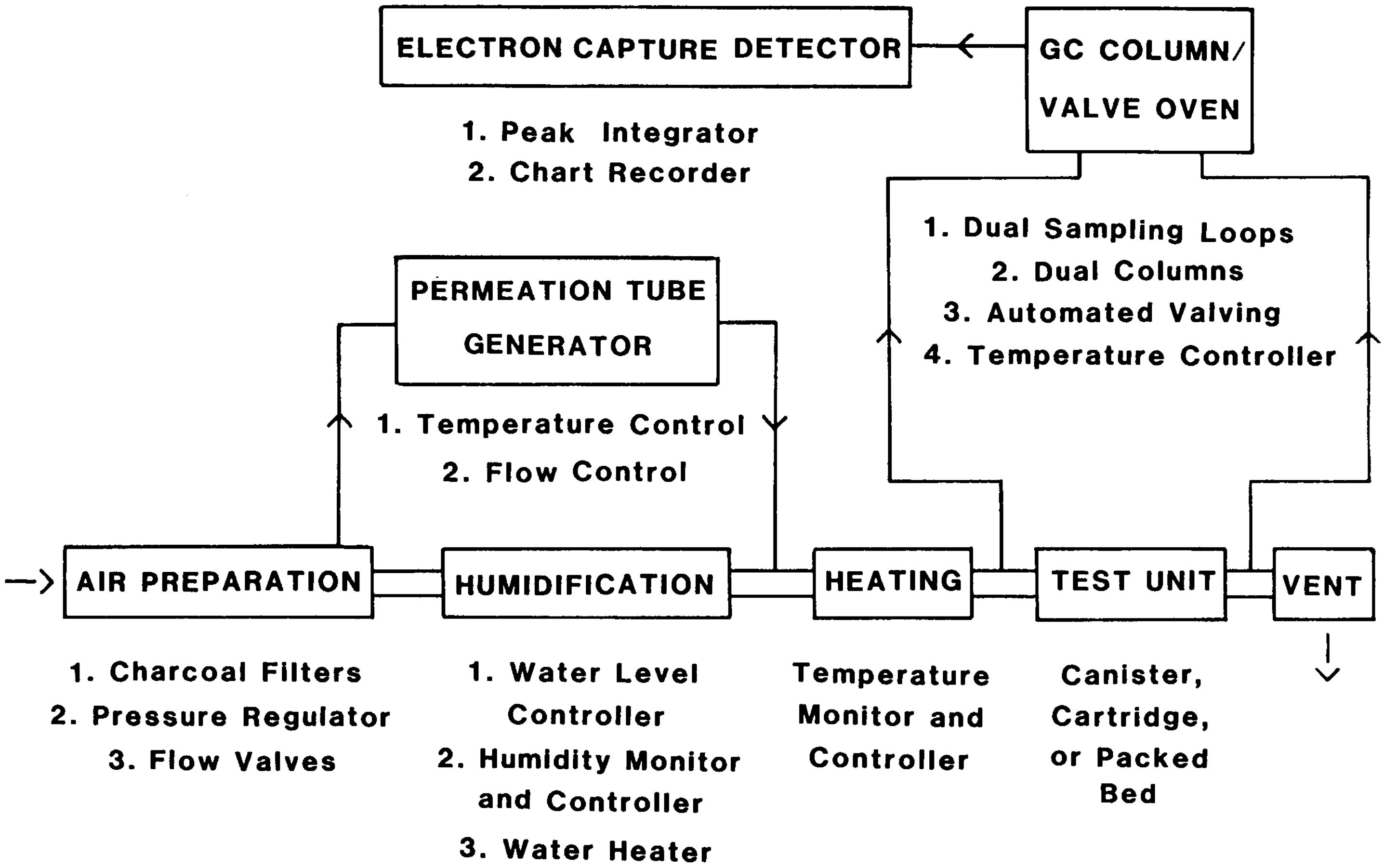

Figure 1 — Schematic of the apparatus developed for testing cartridges and canisters.

type of canister containing an unimpregnated, activated charcoal (Mine Safety Appliances Co., MSA, type GMA) were used in these studies. Each canister and cartridge had a particulate filter followed by a sorbent bed containing the coarse-grained charcoal. They were mounted and sealed to the test apparatus using glass O-ring joints of the proper diameters.

Penetration and Service Life Results

In one set of experiments methyl iodide penetration vs time curves were measured for fresh (unequilibrated) units. Figures 2-4 show the results for three or four temperatures and the three types of cartridges and canisters at 50% RH. For charcoals with TEDA-impregnant, the curves (Figures 2-3) approach an equilibrium penetration with time. The initial penetration increases at each temperature are due to deactivation of TEDA reaction sites by water vapor. Methyl iodide amounts are so small relative to the amount of TEDA that the deactivation by methyl iodide is insignificant. Therefore, when an equilibrium is reached between water vapor of the incoming air and TEDA on the charcoal, the penetration of methyl iodide also reaches an equilibrium value, determined by how rapidly and completely the methyl iodide is removed as it passes through the bed. This kinetically (contact time)-controlled contaminant removal is characteristic of chemisorption or catalysis. For unimpregnated charcoal, the curves (Figure 4) show the more typical, rapidly increasing penetration with time characteristic of capacity-controlled removal (physical adsorption). The fewer adsorption sites are deactivated significantly by both water and methyl iodide. In all cases the penetration curves were shifted to higher penetration values at higher temperatures and constant relative humidity (but higher absolute humidities).

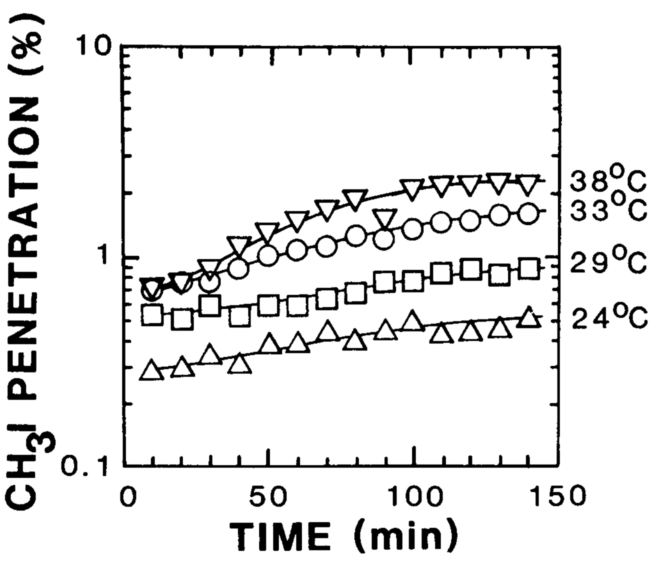

Figure 2 — Air temperature and corresponding absolute humidity effects on methyl iodide breakthrough curves at 32 L/min and 50% RH for Scott 642-TEDA-H cartridges containing 5% TEDA-impregnated charcoal.

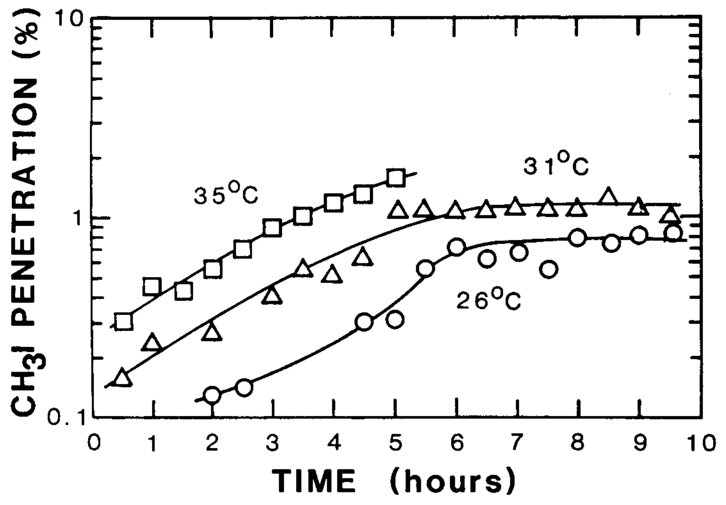

Figure 3 — Air temperature and corresponding absolute humidity effects on methyl iodide breakthrough curves at 64 L/min and 50% RH for MSA prototype canisters containing 2% TEDA + 5% KI$_3$-impregnated charcoal.

When logarithms of penetration percents at selected times for the TEDA charcoals were plotted against temperatures in Figure 5, apparently straight lines were obtained. The slopes of these lines correspond to approximately doubling the penetration for each 5°C (9°F) increase in temperature and corresponding increase in absolute humidity. The penetration increases with temperature for the unimpregnated charcoal were at least twice as large, but were difficult to quantitate due to less overlap of the curves in Figure 4.

The shifts of penetration curves with increasing temperature and corresponding increases of absolute humidity at constant relative humidity also resulted in shortened service lives (breakthrough times at selected penetration values). Figure 6 shows one sample of this effect. Table I summarized the effect for all three cartridges and canisters studied. The effects were quite significant, up to an average 15% decrease in service life for each °C increase (8% per °F). In one case (2% TEDA + 5% KI$_3$ in Figure 6), the temperature effect appears to have varied with the penetration fraction selected to define service life.

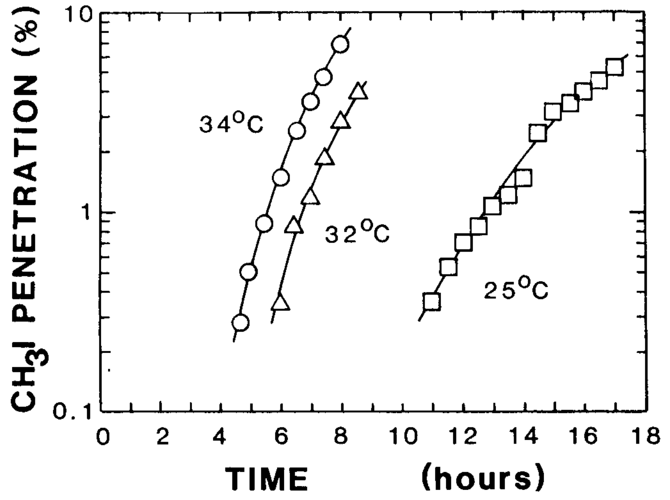

Figure 4 — Air temperature and corresponding absolute humidity effects on methyl iodide breakthrough curves at 64 L/min and 50% RH for MSA GMA canisters containing unimpregnated, activated charcoal.

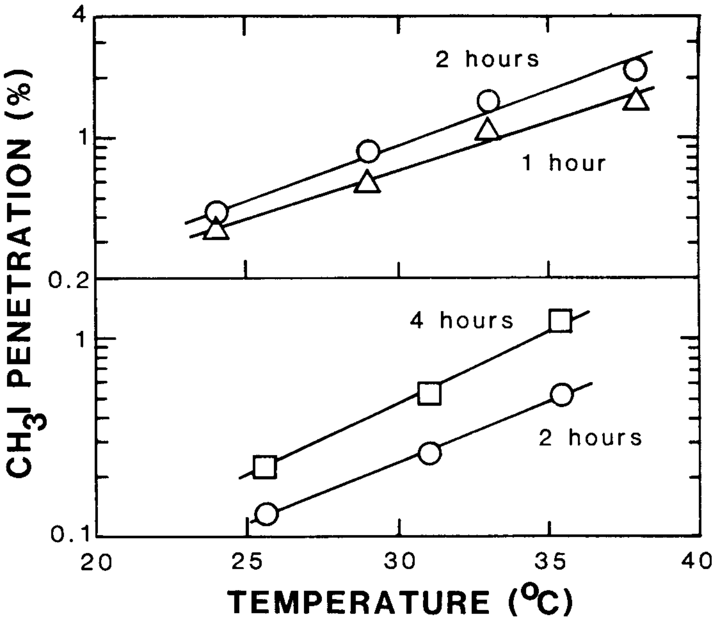

Figure 5 — Effects of air temperature and absolute humidity on methyl iodide penetration at selected times after initiating flows of 50% RH air. Upper graph: Scott cartridge 642-TEDA-H (5% TEDA) at 32 L/min. Lower graph: MSA prototype canister (2% TEDA + 5% KI$_3$) at 64 L/min.

Dew point (absolute humidity or water vapor concentration) was kept constant in another series of experiments with this same canister. Service lives increased significantly with increasing temperature (Figure 7). This is due to the combined effects of less water adsorption (air/charcoal equilibrium shift) and enhanced reaction of methyl iodide with

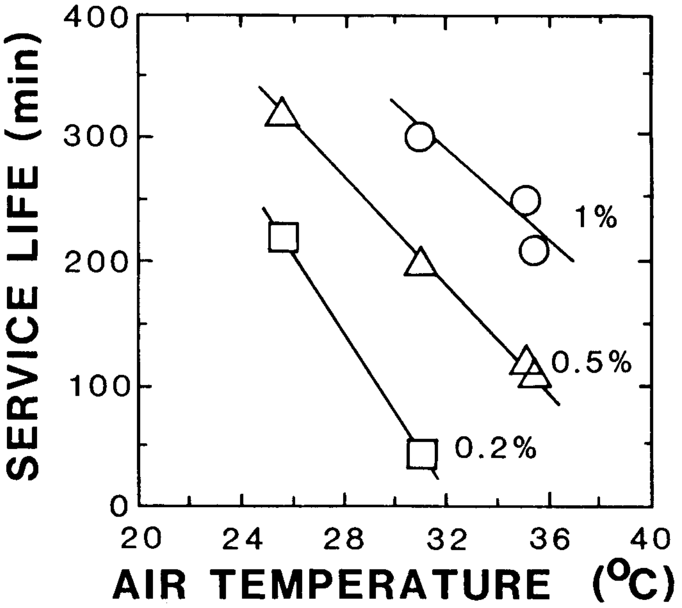

Figure 6 — Effects of air temperature and absolute humidity on service life at three penetrations for constant 50% RH and the MSA prototype canister (2% TEDA + 5% KI$_3$).

TABLE I
Temperature (and Absolute Humidity) Effects on Service Lives at Constant Relative Humidity

Charcoal Type	Relative Humidity (%)	Temperature Range (°C)	Methyl Iodide Penetration (%)	Service Life Decrease (% per °C increase)
2% TEDA + 5% KI_3	52	30-35	1	4
	50	31-35	1	4
		26-35	0.5	7
		26-31	0.2	15
Activated	50	25-34	1	7
	70	25-30	50	5
		25-30	10	5
		25-30	1	5
5% TEDA	50	29-38	1	9

TEDA-impregnant. Average increases in service lives at 1% penetration were 12% per °C at 19°C dew point and 3% per °C at 24°C dew point over the range 25-35°C.

Humidity Heating

The adsorption of water vapor from air passing through charcoal-packed canisters and cartridges was observed to heat them noticeably. Since this occurred whether the charcoal was TEDA-impregnated or not, the effect must be due at least largely to physical adsorption of water. Temperature increases of air passing through fresh Scott cartridges (642-TEDA-H) containing 5% TEDA-impregnated charcoal were measured by placing thermocouples upstream and downstream of the units. Measurable (±0.2°C) temperature rises at 32 L/min airflow and three humidities, shown in Figure 8, continued up to 340 minutes. The maximum increase observed was 10°C for the highest (85%) relative humidity at about five minutes from initial exposure. At 50% RH the temperature also increased significantly, up to 5°C above ambient. At 30% RH the increase was negligible, but measurable, indicating the charcoal was originally drier than it would have been at 30% RH equilibration.

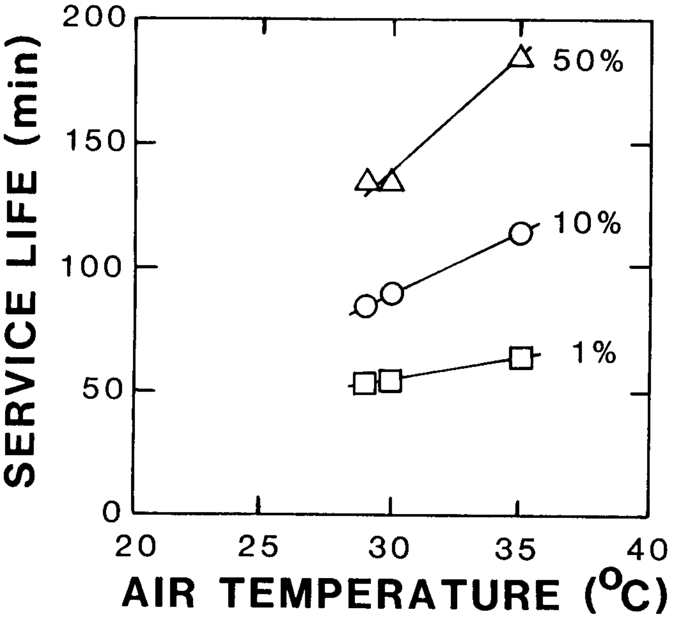

Figure 7 — Effect of air temperature on service life at three penetrations for constant 24°C dew point and the MSA prototype canister (2% TEDA + 5% KI_3).

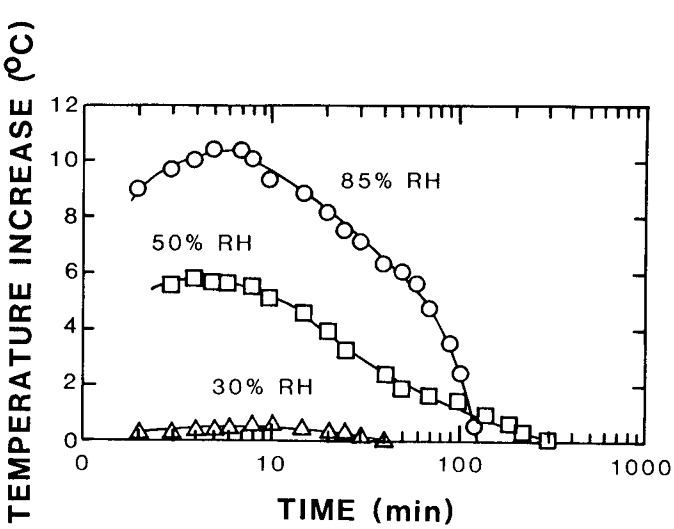

Figure 8 — Humidity heating effects for Scott 5% TEDA cartridges at 32 L/min airflow.

Dew points were measured for air leaving test cartridges as well as for air entering them. This allowed determination of rates of water vapor adsorption at times throughout an experiment. Temperature increases were proportional to water vapor concentration decreases. This relationship was used to calculate heats of water adsorption ranging from 4 to 6 kcal/mole.

Equilibrium Penetrations

When sorbent in a cartridge reaches equilibrium with the humidity in the air passing through it, there is no longer a heating effect due to water adsorption or reaction with impregnants, and ambient temperature effects can be studied without this complication. Equilibrium penetrations would not change with time, since removal of methyl iodide is kinetically controlled by reaction with a large excess of TEDA-impregnant. In one series of experiments, two Scott 642-TEDA-H (5% TEDA) cartridges were equilibrated at 32 L/min airflow within the ranges of 26.4-38°C and 50-91% RH (15.1 to 25.7°C dew points) and methyl iodide equilibrium penetrations were measured. The results of these experiments are given in Table II. For the first three experiments, done with one cartridge at nearly constant temperature, the penetration fraction increased with increasing dew point and relative humidity. The other seven experiments used a second cartridge of the same kind. At constant dew point, *i.e.*, at constant water vapor concentration, the penetration decreased with increasing temperature and decreasing relative humidity. At constant relative humidity, penetration increased with increasing temperature and dew point.

TABLE II
5% TEDA Cartridge Penetrations at Equilibrium

Temperature (°C)	Dew Point (°C)	Relative Humidity (%)	Penetration Fraction	Water Vapor Pressure (torr)[A]
26.6	15.3	50	0.0239	26.117
26.9	21.1	71	0.0777	26.583
27.3	25.7	91	0.1438	27.215
26.3	21.6	75	0.0534	25.661
30.7	21.6	58	0.0327	33.123
34.3	21.6	48	0.0211	40.570
26.4	15.1	50	0.0127	25.812
32.5	20.7	50	0.0233	36.684
34.5	22.5	50	0.0284	41.023
38.0	25.7	50	0.0356	49.692

[A] Reference 6.

Discussion

These experiments have demonstrated that temperature and humidity can both affect penetration of a vapor contaminant and service life of a charcoal bed cartridge or canister. Since temperature, relative humidity, and absolute humidity (water vapor concentration) are interdependent parameters, their individual effects are difficult to quantify. The detrimental effects of high humidities are generally recognized and controlled in testing. These studies have shown that a difference of even a few degrees at a selected relative humidity can make a significant difference in penetration and service life. Kinetic and equilibrium processes are affected by temperature as well as by water vapor concentrations. The generality of this result for other vapors and sorbents remains to be demonstrated. However, for reproducibility and defensibility of results, it would always be prudent to also control temperature as closely as possible, preferably at an agreed value.

With fresh units exposed to high humidities, there is an additional effect of heating due to water vapor adsorption. Heating, which apparently can exceed 10°C (18°F), is of practical importance in comfort of the user. This effect should receive further study. It also can make a difference in determining service life since service life is temperature dependent. Therefore, it should also be considered in designing quality control and certification tests.

The experiments at equilibrium with inlet humidity were useful in sorting out temperature and humidity effects for the special case of TEDA-charcoal and methyl iodide. If a simple competitive mechanism is assumed for chemisorption of methyl iodide and TEDA deactivation by water vapor:

$$A + B \rightarrow AB \qquad (1)$$

$$B + C \rightleftharpoons BC \qquad (2)$$

where $A = CH_3I$
$B = TEDA$
$C = H_2O$.

Simple kinetic and thermodynamic calculations lead to the expression:

$$\frac{-1}{\ln PF} = \frac{K[C]}{k[B]_o t_c} + \frac{1}{k[B]_o t_c} \qquad (3)$$

where $[\,]$ = concentration
PF = penetration fraction of A
$= [A]/[A]$
K = water vapor equilibrium constant
$= [BC]/[B][C]$
k = first order rate coefficient for A + B
$[B]_o$ = the initial concentration of TEDA
t_c = the time which A in the flowing air is in contact with B in the charcoal bed.

The rate coefficient k and equilibrium constant K should be Arrhenius functions of temperature only such that:

$$k/K = a \exp(-b/T) \qquad (4)$$

where a and b = constants.

The data from the constant temperature experiments with the first Scott cartridge (first three in Table II) were used to test Equation (3). In Figure 9, measured values of $-1/\ln PF$ were plotted against water vapor concentrations [C]. The essentially zero intercept implies that $-\ln PF$ is inversely proportional to water vapor concentration, *i.e.*, inversely proportional to relative humidity at constant temperature. Therefore,

$$-[C]\ln PF = (k/K)[B]_o t_c \qquad (5)$$

$$= [B]_o t_c a \exp(-b/T) \qquad (6)$$

The logarithm of the left side of Equation (5) plotted against 1/T (a Clapeyron plot) should be a straight line. Indeed, when the data for the second cartridge (the last seven experiments of Table II) were plotted in this way (Figure 10), a straight line was obtained, corresponding to the expressions:

$$\ln PF = \frac{-1.37 \times 10^6 \exp(-3020/T)}{\text{water vapor pressure (torr)}} \qquad (7)$$

$$= -0.00111 \exp(5300/T_d - 3020/T) \qquad (8)$$

$$= (-0.111/\%RH) \exp(2280/T) \qquad (9)$$

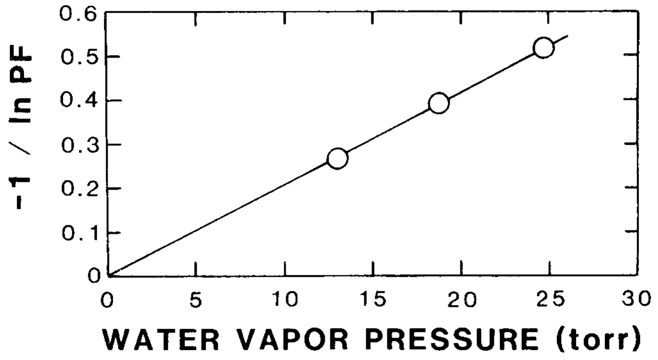

Figure 9 — Plot of data from Table II using Equation (3). Water vapor concentration is expressed as water vapor partial pressure.

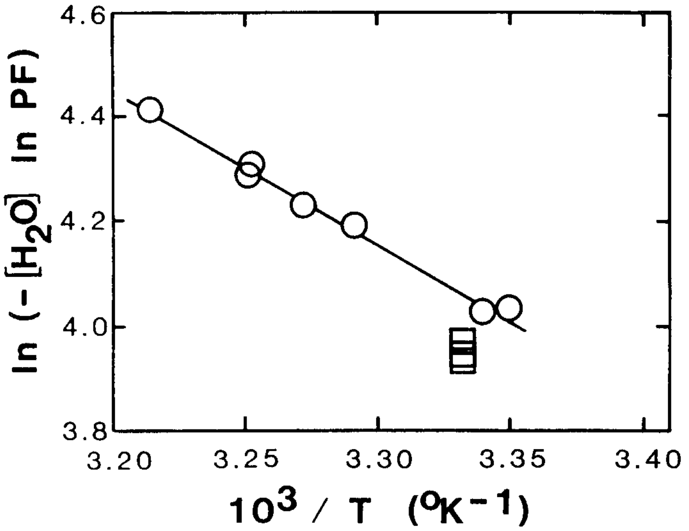

Figure 10 — Clapeyron plot to correlate equilibrium methyl iodide penetrations with dew points and air temperatures.

The exponent $5300/T_d$ (T_d = dew point temperature) comes from the dependence of saturation vapor pressure of water (in torr) on temperature:

$$[C] = 1.239 \times 10^9 \exp(-5300/T) \tag{10}$$

over the range of 10-40°C.(6)

Three data points for the first cartridge, shown as squares in Figure 10, did not fall on the same line as those for the second, supposedly identical, cartridge. This can be accounted for if there was a 24% difference in TEDA-impregnant concentration, $[B]_o$, resulting in different penetration values (compare experiments one and seven of Table II). Such a difference is not surprising, considering the history of prior use of the first cartridge.

Effects of temperature and humidity have been sorted out by these calculations. Admittedly, these data and calculations are for a particular case of one contaminent, methyl iodide, and a special charcoal impregnant, TEDA. However, the above calculations have been useful in confirming the mechanism of the humidity effect and in quantifying the temperature effect for this one case. Similar studies for other systems should lead to a better understanding of the effects that will allow improved predictions of how well sorbent cartridges and canisters work under actual use conditions.

Conclusions

Small changes in ambient temperatures at constant relative humidity or dew point have been shown to produce relatively large effects on penetrations of methyl iodide through fresh and humidity equilibrated canisters and cartridges. This was observed for both TEDA-impregnated and unimpregnated charcoal units. Service lives for fresh units were also significantly affected by temperature. Elevated temperatures can result from water vapor adsorption, affecting both the performance and comfort of the respirator. As shown above, experiments can be designed to sort out effects of ambient temperature and relative humidity. Knowledge of the effects of these parameters can be used to predict the performance of cartridges and canisters at conditions other than those at which they have been tested. Until temperature and humidity effects are better understood, air-purifying respirator cartridges and canister testing should be done at conditions more representative of possible use and at more closely controlled temperatures. Additional data are required to determine how general these effects are for other vapors and sorbents.

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